A Note on Multicomponent Diffusion

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The problem of defining an average diffusion coefficient of a gas arises in the application of the film resistance model for mass transfer to systems involving multicomponent mixtures of simultaneously diffusing gases and in the application of mass, momentum, and heat transfer analogies in such systems. It is shown that, in some cases, integration of the diffusion equation with an average value of the diffusion coefficient will not be valid. An approximate solution of the diffusion equation is obtained with the concentration dependence of the diffusion coefficient taken into account. Some numerical examples are constructed for comparison of this method and several methods for defining an average diffusion coefficient with an exact solution of the Stefan-Maxwell relations.

The problem of defining an average diffusion coefficient of a gas arises in the application of the film resistance model for mass transfer and in the use of mass, momentum, and heat transfer analogies in systems involving multicomponent gas mixtures.

For diffusion of a component through a mixture of gases, in accordance with the concepts of Stefan and Maxwell (5)

$$-\frac{dP_k}{dx} = \sum_{j\neq k} \alpha_{kj} C_k C_j (u_k - u_j) \qquad (1)$$

If D_{kj} is the diffusion coefficient for equimolar counter diffusion in a two-component system of k and j as defined by Fick's law

$$N_k = -\frac{D_{kj}P}{RT}\frac{dy_k}{dx} \qquad (2)$$

then it follows from the above that

$$\alpha_{kj} = \alpha_{jk} = \frac{R^2T^2}{D_{kj}P} \qquad (3)$$

For the case of steady state diffusion combined with bulk gas flow the diffusion equation is generally written in the form

$$N_k = -D_k\frac{dC_k}{dx} + VC_k = -\frac{D_kP}{RT}\frac{dy_k}{dx} + N_t y_k \qquad (4)$$

that is the diffusion effect and the bulk flow effect are considered additive. The above is restricted to steady state unidirectional transfer of ideal gases at constant temperature and pressure. It should be noted that the appropriate velocity is the mole average velocity and not the mass average velocity of the equations of motion. The equations should be modified by the introduction of the appropriate molecular weight ratios before use in mass, momentum, and heat transfer analogies. This Equation (4) is taken as defining D_k. When one introduces a definition

$$\phi_k = \frac{N_k}{N_t} \qquad (5)$$

there results

$$N_k = -\frac{D_kP}{RT\left(1-\dfrac{y_k}{\phi_k}\right)}\frac{dy_k}{dx} \qquad (6)$$

This equation may be integrated over the effective film thickness, and if it is assumed that some average value of the diffusion coefficient can be used, this yields

$$N_k = \frac{\overline{D}_kP}{RTL}\frac{(y_{k1}-y_{k2})}{\left(1-\dfrac{y_k}{\phi_k}\right)_{lm}} \qquad (7)$$

The presence of the logarithmic mean term (film pressure factor divided by the total pressure) allows a correction for the effect of bulk flow on the mass transfer rate. This correction is equivalent to the corrections summarized by Bird, Stewart, and Lightfoot (*2*), where the mass transfer coefficient in the limit of $N_t = 0$ is corrected for finite total mass transfer.

In terms of the usual mass transfer coefficient defined by the equation

$$N_k \equiv k_g P (y_{k1} - y_{k2}) \qquad (8)$$

this yields

$$k_g = \frac{\overline{D}_kP}{RTL(P_f)_{lm}} \qquad (9)$$

as the expression for the mass transfer coefficient under the assumption of a film resistance model.

The individual diffusion coefficients are usually known experimentally or can be estimated, as for example from the results of kinetic theory obtained by Hirschfelder, Bird, and Spotz (*4*), and are known to vary only slightly with composition. Substituting Equations (3) and (5) into the Stefan-Maxwell relation (1) one obtains

$$-P\frac{dy_k}{dx} = \sum_{j\neq k}\frac{R^2T^2}{PD_{kj}}\left(\frac{PN_k}{RT}\right)\left(y_j - y_k\frac{\phi_j}{\phi_k}\right) \qquad (10)$$

and

$$N_k = -\frac{P}{RT\displaystyle\sum_{j\neq k}\left(y_j - y_k\frac{\phi_j}{\phi_k}\right)\frac{1}{D_{kj}}}\left(\frac{dy_k}{dx}\right) \qquad (11)$$

That is

$$D_k = \frac{\left(1-\dfrac{y_k}{\phi_k}\right)}{\displaystyle\sum_{j\neq k}\left(y_j - y_k\frac{\phi_j}{\phi_k}\right)\frac{1}{D_{kj}}} \qquad (12)$$

is obtained as an exact expression for D_k at any point in the film under the assumption of validity of the Stefan-Maxwell relation. Equation (12) is the special one-dimensional case of the general tensor expression for D_k (*1, 3*).

Wilke (*7*) has presented approximate methods for estimating $\overline{D}_k$ when several components are diffusing simultaneously. The use of Wilke's definitions results, when rearranged, in

$$\overline{D}_k = \frac{\left(1-\dfrac{\overline{y}_k}{\phi_k}\right)}{\displaystyle\sum_{j\neq k}\left(\overline{y}_j - \overline{y}_k\frac{\phi_j}{\phi_k}\right)\frac{1}{D_{kj}}} \qquad (13)$$

It is evident, by comparison with Equation (12), that the definitions of Wilke correspond to an average value in terms of arithmetic mean compositions. An approximate method for obtaining an average value of D_k for a three-component system is also suggested by Bird, Stewart, and Lightfoot (*1*) based on the exact relations (12) expressed in terms of concentration gradients rather than ratios of mass transfer fluxes. Its use eliminates the trial and error generally involved in obtaining the mass transfer ratios if the over-all average concentration gradients are used rather than the more correct point values.

However the use of this above average, or any average value of D_k, may

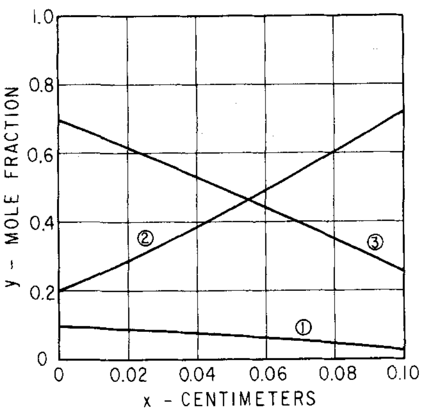

Fig. 1. Composition vs. distance, example 1.

cause the integration of Equation (6) to be divergent. This will be true for situations for which y_k is equal to ϕ_k at some point in the interval. For these cases $(1 - y_k/\phi_k)$ will change signs in the interval, and the logarithmic mean film pressure factor is no longer defined. [If the Cauchy Principle Value of the integral from Equation (6) exists, as it will in most cases, it may be used to redefine the logarithmic mean. It will be seen that this may lead to results which are in considerable error.] The difficulty arises only because of the use of an average value of D_k; otherwise the term $(1 - y_k/\phi_k)$ in the numerator of Equation (12) will cancel at every point the same term in the denominator of Equation (6). Also the problem does not arise when D_k is constant or nearly so, as in this case there can be no solutions for which y_k is equal to ϕ_k within the film.

The solution of the problem lies, in the most general case, in the solution of the simultaneous differential equations arising from the application of the Stefan-Maxwell relation to each component in turn plus one (or perhaps several) additional relations between the mass transfer rates. In most cases this will involve considerable labor because the ratios of the rates of mass transfer, ϕ_j, must be found by successive trial and error or through the combination of many independent numerical solutions of the differential equations.

TABLE 1. MASS TRANSFER COEFFICIENT

Component	Mole fraction		$kg \times 10^5$ — mole/sq. cm.-sec.-atm. Method				
	$x = 0$	$x = L$	1	2	3	4	5
1	0.100	0.033	(−99.4)*	(−55.2)*	(12.4)*	43.8	43.6
2	0.200	0.721	58.5	53.1	57.6	65.0	61.7
3	0.700	0.246	188.2	182.8	177.3	178.1	192.8

* Required redefinition of log-mean film pressure factor.

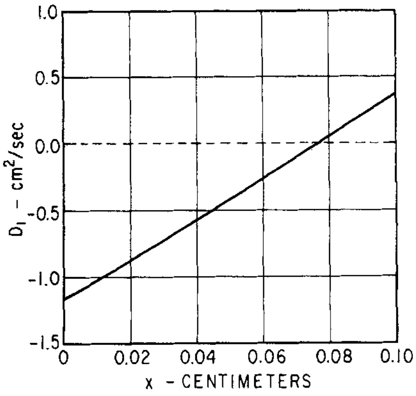

Fig. 2. Diffusion coefficient vs. distance, component 1, example 1.

An approximate solution may be found as follows. From Equation (6)

$$N_k = -\frac{P}{RTL}\int_{y_{k1}}^{y_{k2}} \frac{dy_k}{\sum\limits_{j\neq k}\left(y_j - \frac{y_k\phi_j}{\phi_k}\right)\frac{1}{D_{kj}}} \tag{14}$$

When one uses

$$y_k + \sum_{j\neq k} y_j = 1 \tag{15}$$

there results

$$\sum_{j\neq k}\left(y_j - \frac{y_k\phi_j}{\phi_k}\right)\frac{1}{D_{kj}} = \frac{1}{D_{ks}} - y_k\left(\frac{1}{D_{ks}} + \sum_{j\neq k}\frac{\phi_j}{\phi_k D_{kj}}\right) + \sum_{j\neq k,s} y_j\left(\frac{1}{D_{kj}} - \frac{1}{D_{ks}}\right) \tag{16}$$

where s may be any component other than k. For a two-component system the last term is zero, and the expression is linear in y_k. For many components, and with D_{ks} chosen as an intermediate value, the last term in Equation (16) will have some positive and some negative values, tending to cancel. Even when these terms do not cancel, the values of the y_j are strictly bounded by zero and one and are usually known at the two ends of the interval. If the last term in Equation (16) is taken to be approximately linear in y_k, the entire expression will be approximately linear in y_k. With this approximation there results, upon integration of Equation (14)

$$N_k \cong \frac{P(y_{k1} - y_{k2})}{RTL\left[\sum\limits_{j\neq k}\left(y_j - \frac{y_k\phi_j}{\phi_k}\right)\frac{1}{D_{kj}}\right]_{lm}} \tag{17}$$

or in terms of a mass transfer coefficient

$$kg \cong \frac{1}{RTL\left[\sum\limits_{j\neq k}\left(y_j - \frac{y_k\phi_j}{\phi_k}\right)\frac{1}{D_{kj}}\right]_{lm}} \tag{18}$$

A numerical example will help to illustrate the points in the above presentation. The following values were chosen arbitrarily for a three-component system, the composition at $x = L$ being fixed by the exact solution of the Stefan-Maxwell relations:

$P = 150$ mm. Hg (0.197 atm.) $T = 40$°C. (313°K.)

$$\frac{RTN_t}{P} = 15.0 \text{ cm./sec. or } N_t = 11.526 \times 10^{-5} \text{ g.-moles/sec.-sq. cm.}$$

		at $x = 0$
$L = 0.1$ cm.		
$D_{12} = 1.000$	$\phi_1 = 0.05$	$y_1 = 0.1000$
$D_{13} = 5.000$	$\phi_2 = -0.55$	$y_2 = 0.2000$
$D_{23} = 3.000$	$\phi_3 = 1.50$	$y_3 = 0.7000$

With these values an exact solution of the set of simultaneous differential equations yields

$$y_1 = 0.0500 - 0.0562 \exp.(+5.122x) + 0.1062 \exp.(-3.222x)$$
$$y_2 = -0.0550 + 0.6257 \exp.(+5.122x) - 0.3707 \exp.(-3.222x)$$

and

$$y_3 = 1 - y_1 - y_2$$

so that at $x = L$ the film thickness

$$y_1 = 0.0331$$
$$y_2 = 0.7210$$
$$y_3 = 0.2459$$

A plot (Figure 1) of mole fraction vs. distance shows no unusual behavior. However the diffusion coefficient for component 1 defined by Equation (4) is negative over a considerable region (Figure 2) and thus does not have the usual physical significance of a diffusion coefficient. It tends to become only a mathematical entity.

Component 1 is of special interest because ϕ_1 is between y_1 at $x = 0$ and y_1 at $x = L$. Values of the mass transfer coefficients are compared below (Table 1) with the value corresponding to the true solution of the Stefan-Maxwell relations under the assumption that the true values of the mass transfer ratios ϕ_k and ϕ_j are known. In a particular case these would have to be found by trial and error, first by assuming values of N_j, calculating ϕ_j and then recalculating N_j until the approximate Equation (7) or (17) is satisfied. It should be noted that use of Equation (7) can never produce a value of ϕ_k between y_{k1} and y_{k2} and will therefore produce additional error in the calculated rates for the other components which is not evident in the comparison below.

TABLE 2. MASS TRANSFER COEFFICIENT
$kg \times 10^5$ g.-mole/sq. cm.-sec.-atm.

	Method 1	2 and 3	4	5
kg × 10^5	137.8	80.7	84.3	84.9
error %	62.4	4.9	0.7	

The following methods for estimating the mass transfer coefficients are compared.

1. Use of Equation (9) with the diffusion coefficients averaged with respect to arithmetic mean mole fractions.
2. As in 1 with the diffusion coefficients averaged for each component as if the other components were stagnant [Equation (13) with $\phi_k = 1$, $\phi_j = 0$ for $j \neq k$].
3. As in 1 with the average diffusion coefficient from Wilke's film pressure factor method [Equation (13)].
4. Use of Equation (18) as developed in this paper.
5. Exact or true value from the solution of the Stefan-Maxwell relations.

At $x = 0$	At $x = L$

Those cases for which the logarithmic mean film pressure factor is undefined have been indicated with an asterisk, and values were calculated with the principle value of the integral from Equation (6). (See Table 1.)

It is evident that while the film pressure factor method, method 3 above, is an improvement over the crude forms, methods 1 and 2, it is still in considerable error for component 1. This is because, as pointed out earlier, no average value of D_k will give a satisfactory result for cases in which $\phi_k = y_k$ at some point in the film. For the other components all of the methods give reasonable results for the values chosen here.

This would lead to the conclusion that Equation (4) is no longer satisfactory for defining D_k for component 1 and that for cases of this type the mass transfer coefficient has more significance than an average diffusion coefficient. The problem is avoided if it is kept in mind that Equation (4) defines D_k at a point and that with respect to integration the ratio D_k/P_f has more significance than either D_k or $(P_f)_{lm}$ separately.

While the above example clearly shows the conditions under which the use of an average diffusion coefficient breaks down, it is not a convincing test of the general applicability of Equation (18) because of the nearly linear concentration profiles. An additional example was constructed in which the curvatures of the concentration profiles are more pronounced (Figure 3). The figures given below correspond to diffusion of component 1 through a stagnant film of components 2 and 3 and were chosen for convenience, except for the values of y at $x = L$ which are from an exact solution. The pressure, temperature, and mutual diffusion coefficients are the same as for the previous example:

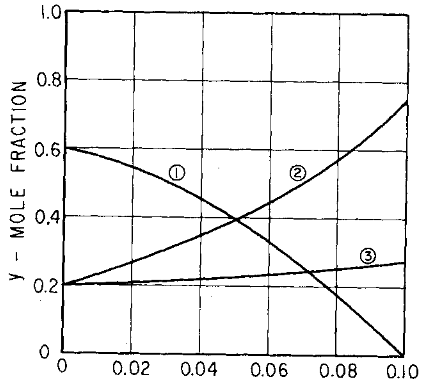

Fig. 3. Composition vs. distance, example 2.

$$\text{for } N = 10.06 \times 10^{-5} \frac{\text{g.-moles}}{\text{sec.-sq. cm.}}$$

$y_1 = 0.600$	$y_1 = 0.000$
$y_2 = 0.200$	$y_2 = 0.738$
$y_3 = 0.200$	$y_3 = 0.262$

The mass transfer coefficients for component 1 are compared as before. For this case methods 2 and 3 reduce to the same equations. (See Table 2). In this example only method 1 is in considerable error.

In summary, for situations involving simultaneous diffusion of several components it is generally proper to consider the concentration dependence of the diffusion coefficient rather than to make use of an average value. It is suggested that the approximate relation, Equation (17), will be useful for many engineering applications, especially in situations where some relationships between the mass transfer rates are determined by other considerations, for example chemical reaction. For other cases the trial-and-error or iterative procedure required to determine the mass transfer ratios may or may not converge to the values which are true (approximate) solutions of the Stefan-Maxwell relations. For example $N_k = 0$ is always a solution of Equation (17) but may not be a solution of the Stefan-Maxwell relations. This difficulty is considered in more detail by Toor (6).

The use of Equation (17) is equivalent to using an average value of the ratio (D_k/P_f) rather than averaging D_k and P_f separately. The result is exact if there are only two components or if all of the binary diffusion coefficients are equal.

ACKNOWLEDGMENT

The author is grateful to the Dow Chemical Company and the National Science Foundation for financial assistance.

NOTATION

C_k, C_j = concentration of components k and j, g.-mole/cc. sq. cm.
D_k = effective diffusion coefficient for component k, sq. cm./sec.
D_{kj} = diffusion coefficient for equimolar counter diffusion of components k and j, sq. cm./sec.
$\overline{D_k}$ = average value of D_k with respect to integration, sq. cm./sec.
k_g = mass transfer coefficient, mole/sq. cm.-sec.-atm.
L = effective diffusion path length, cm.
N_k, N_j = mass transfer rates of components k and j, g.-mole/sq. cm.-sec.
N_t = total mass transfer rate, g.-mole/sq. cm./sec.
P = total pressure, atm.
P_k = partial pressure of component k, atm.
P_f = film pressure factor, equal to $P(1 - y_k/\phi_k)$, atm.
R = gas constant, equal to 82.06, atm.-cc./g.-mole-°K.
T = temperature, °K.
u_k, u_j = net velocity of components k and j, cm./sec.
x = distance coordinate, cm.
y_k, y_j = mole fractions of components k and j, dimensionless
$\bar{y}_k, \bar{y}_j$ = arithmetic mean mole fractions based on the terminal conditions of the film
α_{kj} = proportionality constant in the Stefan-Maxwell relation, atm.-sec.-cm.^{4}/g.-mole^2
ϕ_k, ϕ_j = ratios of mass transfer rates, dimensionless

Subscripts

1,2,3 = property of component 1, 2, and/or 3
k, j, s = property of component k, j, and/or s
k_1, k_2 = property of component k evaluated at $x = 0$ and $x = L$ respectively
lm = logarithmic mean

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Manuscript received October 9, 1959; revision received April 26, 1960; paper accepted April 27, 1960.